Local structure probes of nanoscale heterogeneity in crystalline materials

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In the conventional model of condensed matter increasing numbers of defects break down the order and ultimately convert perfect periodic crystals into aperiodic glasses. Local structure probes of a variety of materials with non-stoichiometric compositions, multiple degenerate ordering modes, or other symmetry breaking factors identify multiple ordered arrangements of atoms that render the materials heterogeneous on the nanometer scale. While exerting apparently negligible effects on bulk properties, this heterogeneity or phase separation does influence correlated or collective properties such as magnetism and phase stability.

Keywords: Nanoscale, heterogeneity, local structure, XAFS, PDF, pair distribution

1. Introduction

The structure:function principle is easily demonstrated in simple, i.e., calculable, periodic systems. The determination of the coupling between the arrangement of the atoms and materials' properties is much more difficult in materials with aperiodic compositions or charge distributions. The attributes of such complex materials not only depend on more parameters (some of which may not even be known initially) but are also subject to the likelihood that some of these parameters will be linked, resulting in nonlinear and discontinuous behavior. Nevertheless, the assumption that structure:function relationships rigorously apply even to complex materials continues to motivate the study and analysis of their structures on the atomic scale even when the expected correlations between structure and the properties of interest will only be poorly understand or must remain purely empirical.

The crucial division between simplicity and complexity is whether the different elements or ions that reside in a particular lattice position behave similarly in an averaged fashion or retain their original identities and exhibit pair-specific interactions. If the former, then their effects on the structure and its stability will be cumulative, linear, and easy to predict. If the latter, then complex, nonlinear, even discontinuous or critical types of behavior are possible, culminating in nanoscale heterogeneity or phase separation (Fig. 1) (Conradson, 1998; Colyer et al., 1997; Bauer et al., 1996; Tyson et al., 1996), which is associated with interesting correlated behaviors of electrons (e.g., high temperature superconductivity (Tranquada et al., 1995; Bianconi et al., 1996) and colossal magnetoresistance (Chen et al., 1999)) and atoms (phase stability) (Conradson, 1998). Such, commingled, differently ordered (as opposed to disordered), incommensurate and aperiodic arrangements of atoms could be driven by nanoscale fluctuations in composition, charge, and local strain that perturb the long range forces that typically determine the crystal structure in conventional materials. These local effects may occur naturally because of the random distribution of susbstitutional elements in non-stoichiometric compounds, but may also result or be enhanced by collective interactions among putatively isolated defect sites. The small size of these domains (at or below the Bragg diffraction limit) as well as their lower dimensionality and poor coherence prevent them from diffracting elastically even while they may comprise up to one-fourth of the material. Their presence, however, is revealed in local structure measurements because they are not glassy. Within the different, aperiodic arrangement of atoms comprising the second domain there is still a rigid ordering that results in highly correlated atom pairs well past the nearest neighbors.

2. Supporting Experimental Results

One example of ion specific interactions in non-stoichiometric compounds is offered by quaternary, Y-Er-Ce/U, cubic stabilized zirconias (CSZ). An interesting pattern is elucidated by multishell curve-fits of $\chi(k)$ supported by comparisons with the spectra of pure ZrO_2. The O nearest neighbors around the Zr and Y are highly distorted whereas the cation shell is relatively symmetric, whereas the converse is observed for the Er despite its virtual identity in size and charge to Y. This suggests multiple modes for local strain relief of the lattice that are highly sensitive to the specific details of the site. On substitution of Ce by U, the Zr and Er retain the principal features of their local structures while accommodating the slightly larger cation by an expansion of the cation sublattice and longer distances to this and more distant shells (Ping et al., 1993; Ping et al., 1994). In contrast, the cation shell of Y becomes more Gaussian and its the O nearest neighbor distribution becomes much more complicated than in the Ce compound. This result implies that the Y and U local environments interact strongly, probably encouraging the formation of Y-U second nearest neighbor moieties within the host lattice. Cooperative behaviour of this type has previously only been reported for cations smaller than Zr^{4+} (Ping et al., 1994), so this finding suggests that U (and other actinides?) experience novel kinds of interactions with the host lattice. In addition, whereas the Ce-O distance is contracted from CeO_2, the U-O distance is not contracted from UO_2 so that the U differs from Ce in not experiencing comparable compression in the nearest neighbor O shell.

Organization of local distortions into domains has been observed in Pu-doped synroc compounds and magnetic alloys. Anomalous x-ray Pair Distribution Function (PDF) measurements corroborated the identification by XAFS of a 5.5 Å distance between most of the Pu-Pu in $Ca_{0.8}Pu_{0.2}HfTi_{1.8}Al_{0.2}O_7$. Since there are no Ca-Ca pairs with this distance in the crystallographic structure then the local strain fields around the Pu are either causing the Pu ions to aggregate into Ca and next nearest neighbor Zr positions, despite the substitution for Ca, or to order into a second domain that is distorted so that the Pu on the Ca sites have that separation. Thin film $Pt_{0.74}Co_{0.26}$ displays substantial magnetic anisotropy despite diffraction patterns that show the cubic Au_3Cu type of lattice. XAFS measurements on oriented samples have revealed the presence of large numbers of Co-Co nearest neighbors perpendicular to the magnetization direction when none should occur in the cubic structure. The magnetic properties and local structure are consistent with non-diffracting domains of layered Co-Pt that form normal to the growth direction (Tyson et al. 1996). The same type of chemical ordering in NiMn results in a tegragonal distortion and antiferromagnetism (Farrow et al., 1996). The latter can occur

before tegragonal splitting of diffraction peaks is displayed. XAFS measurements on this system were performed on this system and the curve-fitting results were enhanced by phase shift analysis and modeling of the third-fourth shell region in R space. Despite reduced amplitudes, the phase shifts showed a strong correlation with the exchange coupling of the samples and were aligned with the calculations of highly ordered materials, implying highly developed short range tetragonal order (Conradson, 1998). This separation between short and long range order therefore appears to be not uncommon in both non-stoichiometric compounds and stoichiometric materials with multiple ordering mechanisms.

Although we have many more examples of these effects in, e.g., protonated and super-oxygenated Pu(IV) oxide and manganites, the most incisive one we have at present is the δ-stabilized Pu alloy system (Conradson, 1998). Several elements, including Ga, In, Ce, Am, Al, and Sc, stabilize the low density fcc δ phase to ambient temperature and below beginning at concentrations of 1–5 atomic-% (American Nuclear Society, 1980). At compositions only slightly above those required for the stabilisation a martensitic transformation of a fraction of this metastable material to the monoclinic high density α phase can be induced at lower temperatures and elevated pressures. We have performed multiple edge XAFS as well as some XRD and x-ray PDF measurements on dozens of mostly Ga but also several In and Ce-stabilized δ Pu samples, both newly prepared and aged. Using these data, we have been able to determine the characteristics of the local strain fields around the trace elements, showing that the PuGa alloys go from meta- to fully stable when the strain fields around the Ga come into contact on average. However, our most interesting finding is of heterogeneity in metstable alloys that is common to all three stabilizers. An identical pattern of non-δ Pu-Pu distances is found by the PDF. In addition, a few samples have displayed a second diffraction pattern at low temperature. The space group Fm-3m with a=5.0 Å gives atom positions that correspond well with the distances found by the XAFS and PDF from 5 Å. Below that, the local structure probes exhibit a prominent Pu shell at 3.8 Å but nothing at the 3.5 Å distance expected from this diffraction pattern. However, if this first shell was split by a Bain transformation that also conserved the 3.25 Å bond length in δ Pu but was predominantly ordered according to the crystallographic data beyond then it would produce exactly this result. We have very recently found a lattice distortion (in two dimensions) that gives this type of PDF while conserving the diffraction pattern. Obviously there must also be some interstitial atoms with short distances to conserve the density, which we have now found in some recent XAFS measurements. These need not affect the diffraction pattern.

Using this information we have developed the schematic structural model depicted in Fig. 2 using a random distribution of Ga except that Ga-Ga nearest neighbor pairs are forbidden. The δ structure is assumed to more readily accommodate the local strain fields around the Ga sites so that it forms around the areas with locally high Ga concentrations. It also readily extends, connecting the δ domains so that they form the coherent host lattice. The second structure, which we call σ, then forms in the areas with locally low Ga concentrations. Domain walls of finite but unknown size form the interfaces between the different types of structures. As the δ-stabilizer concentration increases the volume of the low Ga concentration regions decrease, with a relatively rapid final turn off as the last spaces are filled.

3. Summary

Nanoscale heterogeneous or phase-separated crystals represent an alternative organization mode to the conventional perfect crystal-glass description. We now have definitive local structure evidence in many classes of materials that the atoms are arranged in two (or more) ordered modes, only one of which typically or dominantly diffracts, and that this does affect correlated properties such as magnetism or phase stability. We also have begun to obtain some information about the rules relating these multiple structures, which appear to form without affecting the density or other bulk properties. The possibility of nanoscale heterogeneity as an alternative modality for organizing condensed matter exacerbates the difficulties in structure determination, especially because of the dearth of probes sensitive to aperiodic structures on this scale.
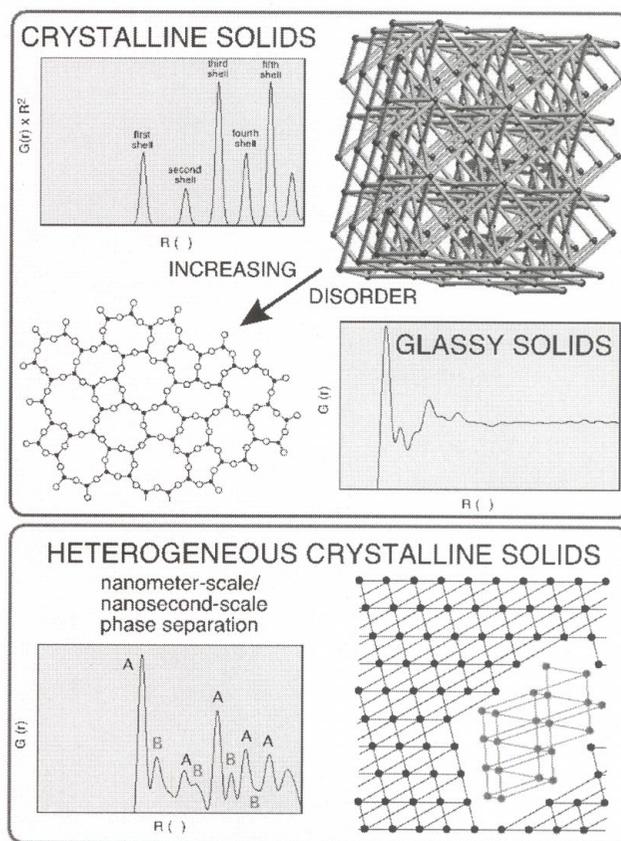
Figure 1
The conventional model of solids (left) has, at one extreme, perfectly ordered crystals with precisely defined lattices and pair distributions extending throughout the entire crystal that, with increasing numbers of displacements and other defects, will ultimately shift to the other extreme, glasses, with only local order that quickly disappears into the average atomic density. An alternative type of behavior (right) occurs when atomic scale fluctuations in composition, charge, and other parameters are sufficiently large to promote the formation within the host crystal of a second, well ordered arrangement of the atoms, giving rise to nanometer-scale heterogeneity or phase separation.
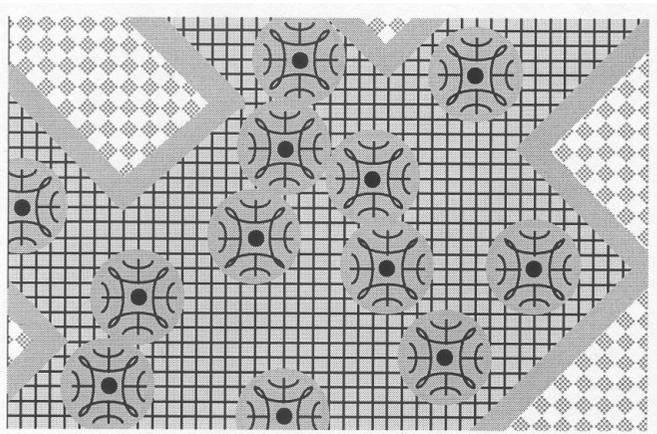
Figure 2
XAFS and x-ray scattering data are consistent with nanoscale heterogeneity in metastable δ Pu alloys. In regions where the concentration of the randomly distributed δ stabilizing element (black dots) is high, the local strain fields around them (curved lines) are more easily accommodated within the δ fcc structure (square lattice). In the separated regions between these strain fields that are above a size threshold the Pu atoms rearrange into the more complicated σ structure (diamonds). The domain walls are of finite but unknown size, possibly much wider than depicted here.

References

Conradson, S. D. (1998). *Appl. Spectr*. **52**, 252A–279A.
Colyer, L.M., Greaves, G.N., Carr, S.W., & Fox., K.K. (1997). *J. Phys. Chem.* **B 101**, 10105–10114
Bauer, E. D., Bridges, F., Booth, C. H., Boyce, J. B., Claeson, T., Brorsson, G., & Suzuki, Y. (1996). *Phys. Rev.* **B 54**, 13354-13360.
Tyson, T. A., Conradson, S. D., Farrow, R. F. C., & Jones, B. A. (1996). *Phys. Rev.* **B 54**, R3702–R3705.
Tranquada, J. M., Sternlieb, B. J., Axe, J. D., Nakamura, Y., & Uchida, S. (1995). *Nature* **375**, 561–563.
Bianconi, A., Saini, N. L., Lanzara, A., Missori, M., Rossetti, T., Oyanagi, H., Yamaguchi, H, Oka, K., & Ito, T. (1996). *Phys. Rev. Lett*. **76**, 3412–3415.
Chen, H., Mori, S., & Cheong, S.-W. (1999). *J. Phys IV, Proc.* **9**, 307-310.
Li, P., Chen, I.-W., & Penner-Hahn, J. E. (1993). *Phys. Rev.* **B 48**, 10074-10081.
Li, P., Chen, I.-W., & Penner-Hahn, J. E. (1994). *J. Am. Ceram. Soc.I* **77**, 118–128.
Farrow, R. F. C., Weller, D., Marks, R. F., Toney, M. F., Horn, S., Harp, G. R., & Cebollada, A. (1996). *Appl Phys. Lett.* **69**, 1166-1168.
American Nuclear Society (1980). *Plutonium Handbook*, *A Guide to the Technology*, edited by O. J. Wick. La Grange Park, Illinois, USA.